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HETEROGENEOUS DESTRUCTION OF NITROUS OXIDE BY CHAR

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Reduction of N_2O by chars from subbituminous Siersza, Piast and Janina coals have been studied in a pressurised reactor at 973 - 1173 K. It has been found that the reaction $N_2O + [C] \rightarrow N_2 + [CO]$ is controlled both by the chemical kinetics and diffusion of N_2O within char particle's pores. The rate constant of the above reaction has been found to be independent of pressure within the examined range of 0.2 – 1.0 MPa.

Key words: pressurised combustion modelling, N_2O reduction.

Heterogena destrukcija dušikovog oksida čađom. Smanjenje N_2O čađom iz subbituminoznih ugljena Siersza, Piast i Janina istraživano je u tlačnom reaktoru pri 973 - 1173 K. Utvrđeno je da brzina reakcije $N_2O + [C] \rightarrow N_2 + [CO]$ ovisi i o kemijskoj kinetici i difuziji N_2O u porama čestica čađe te da je konstanta brzine reakcije neovisna o tlaku u istraživanom području tlakova od 0,2 do 1,0 MPa.

Ključne riječi: modeliranje izgaranja pod tlakom, smanjenje N_2O .

INTRODUCTION

Mathematical modelling of emission of pollutants during coal combustion requires appropriate kinetic data. Pressurised combustion is very attractive for the power industry, not only because it reduces carbon dioxide emissions when applied in combined cycles, but also because less nitric oxide is emitted. However, in the process, no explanation of the mechanism of N_2O reduction has been offered. It is believed that N_2O formed during combustion is reduced over char particles at enhanced pressures [1-4].

Compared with the reaction with NO, reduction of N_2O by carbon and formation of N_2O from coal char have been investigated to only a small extent. These reactions are not so

important for high temperature combustion, but they are very important in a low temperature process like fluidised bed combustion or pressurised combustion. As in the case of NO, formation and destruction of N_2O concurrently take place in the combustor. In the case of N_2O reduction by carbon, it was assumed that N_2 is produced from N_2O without any bond breaking between two nitrogen atoms, although no direct evidence was found [5].

The reaction can be described as a pseudo-first-order reaction. The influence of pore diffusion is likely to be relatively large since the reaction rate is approximately an order of magnitude faster than for a NO reaction over char. Rodriguez-Mirasol et al.

[6] investigated decomposition of N_2O by char. They found that the values of activation energy for the reaction of N_2O and series of chars were within the range of 66-104 kJ mol^{-1} . The values of activation energy for NO were found to be higher (111-181 kJ mol^{-1}). Similar results were obtained by de Soete [7]. He found the values of activation energy within the range of 83-116 kJ mol^{-1} for N_2O and significantly lower values, 138-148 kJ mol^{-1} , for NO and the same chars.

Bonn et al. [8] carried out experiments in fluidised bed boilers within the temperature range of 1133-1173 K and they found that N_2O conversion could be explained by thermal decomposition in the gas phase during the secondary cycle of the CFBS and enhanced by decomposition on solid particles of char in the recirculation cycle. They estimated the activation energy for N_2O decomposition to be 114 kJ mol^{-1} for char obtained from "Gaskohle" coal. In their model of combustion within the temperature range of 1023-1123 K, Goel et al. [9] used the activation energy of 141 kJ mol^{-1} for N_2O destruction, which is similar to the value recommended by Chen et al. [10] (139 kJ mol^{-1}).

Johnsson et al. [11] measured N_2O and NO decomposition rates over char samples from a 12 MW CFB boiler operating at 1073-1223 K. They estimated that the activity of char for N_2O reduction was ten times larger than that for NO decomposition. They also estimated the values of activation energies for various operating conditions to be 101-113 kJ mol^{-1} .

Heterogeneous NO and N_2O formation and destruction mechanisms were presented by Gil [12, 13] in a form suitable for modelling under a broad range of char combustion conditions. The reaction rate constants of the kinetic equations were found to be independent of the combustion pressure. The model was verified on the basis of

experiments in a pressurised combustor, at up to 1.5 MPa. It was found that char-N conversion towards NO decreases, while it increases towards N_2O with an increase in the combustion pressure, which is well reproduced by this mechanism.

Croiset et al. [14] studied the influence of pressure on heterogeneous formation and destruction of NO and N_2O during combustion of char in a pressurised fixed-bed reactor. The experiments were performed at 0.2, 0.6, and 1.0 MPa for temperatures 850 K to 1200 K with char whose parent coal was high volatile bituminous coal (Westerholt). They found that the total pressure had no influence on NO and N_2O formation rates. The work also confirmed that the pressure accelerated decomposition of NO and N_2O over char and that N_2O was more readily reduced over char than NO.

For N_2O reduction, they proposed (for the pressures: 0.2, 0.6 and 1.0 MPa) three different kinetic constants with activation energies: 78, 85 and 91 kJ mol^{-1} , which are lower than kinetic constants suggested by all other authors, and they found them to be pressure-dependent. Later, the same authors (de Soete et al. [15]) did not reject the dependence of the rate constants of heterogeneous reactions on the total pressure for chars produced under the same conditions. Because the char samples used in those experiments were prepared at 0.1 MPa, there should be no reason why the properties of the char are influenced by pressure.

The aim of this research was to check rate constants of the reaction $\text{N}_2\text{O} + \text{C} \rightarrow \text{N}_2 + \text{CO}$ at pressures up to 1.0 MPa where the largest influence of pressure on N_2O emission was observed (Croiset et al. [14]). The rate constants of the reaction $\text{NO} + \text{C} \rightarrow 0.5\text{N}_2 + \text{CO}$ were estimated in the previous work of Tomczek and Gil [16].

EXPERIMENTAL

The experiments were carried out in a pressurised reactor (a volume of $1.88 \times 10^{-3} \text{ m}^3$) as shown in Figure 1. A monolayer sample of 0.5 g char particles (sized 0.8-1.0 mm) was placed in helium gas containing initially 300 ppm of N_2O and heated electrically at the rate of 100 K/s to a final

temperature of 973 to 1173 K. The final heating temperature and the sample's residence time at this temperature were automatically controlled. The maximum deviation from the adjusted temperature within the isothermal period was smaller than $\pm 20 \text{ K}$.

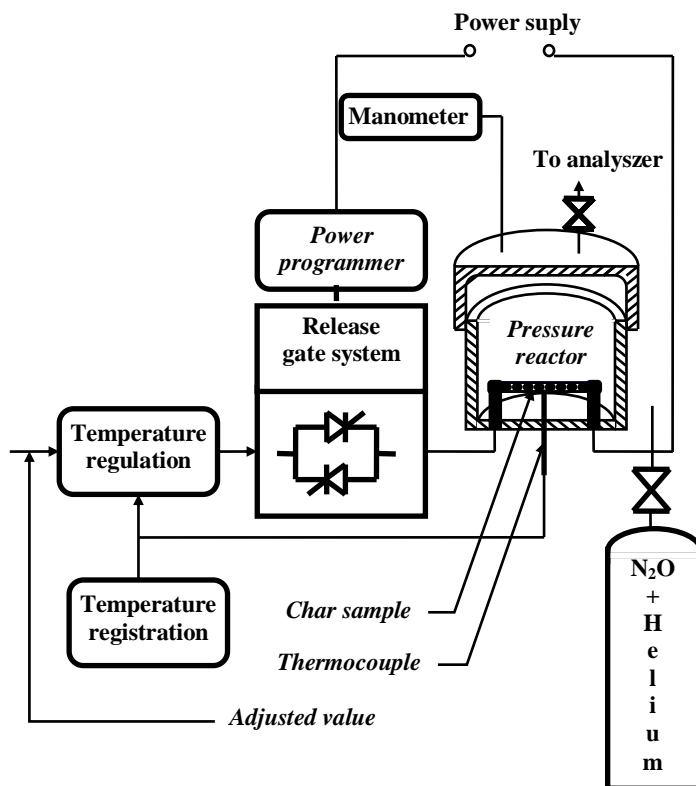


Figure 1. Apparatus
Slika 1. Aparatura

The temperature of the sample was measured by a NiCr-NiAl thermocouple and continuously recorded. The size of the char was chosen to prevent the particles' blow

from the crucible. The total experimental time was 90 s and included both the heating time and the isothermal reaction time.

After the adjusted residence time at the final temperature, the heater was switched off and then N_2O concentration in the reactor gases was measured by a "Maihak" system with a UNOR 610 analyzer. The experiments were performed for three pressure values: 0.2, 0.6 and 1.0 MPa. The char was produced

earlier by coal carbonization in pure helium at 1173 K and 0.1 MPa during the time period of 20 min. The following parent coals were used during the investigations: SIERSZA, JANINA and PIAST. The characteristics of these coals are presented in Table 1, and those of the chars – in Table 2.

Table 1. Characteristics of coals

Tablica 1. Karakteristike ugljena

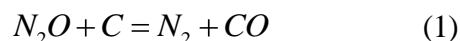
| Enriched coal | W^a % | V^{waf} % | A^{wf} % | C^{waf} % | H^{waf} % | S^a % | N^{waf} % | Porosity ϵ_0 % |
|----------------|------------|----------------|---------------|----------------|----------------|------------|----------------|----------------------------|
| SIERSZA | 2.6 | 37.7 | 6.9 | 77.0 | 5.1 | 2.5 | 1.51 | 15.8 |
| JANINA | 3.2 | 33.9 | 8.1 | 77.6 | 3.3 | 1.1 | 1.34 | 14.6 |
| PIAST | 5.7 | 30.8 | 7.1 | 84.2 | 3.9 | 1.2 | 1.42 | 15.1 |

Table 2. Characteristics of chars

Tablica 2. Karakteristike čađa

| Char | Internal surface area A_c $m^2 kg^{-1}$ | N_c^a % | Porosity ϵ_c % | Real density ρ_c $kg m^{-3}$ |
|----------------|---|--------------|-------------------------------|---|
| SIERSZA | $27.1 \cdot 10^3$ | 0.91 | 40.0 | 1210 |
| JANINA | $16.7 \cdot 10^3$ | 0.79 | 59.3 | 1390 |
| PIAST | $12.5 \cdot 10^3$ | 0.78 | 45.7 | 1320 |

The rate of N_2O heterogeneous reduction in the overall reaction



can be described by the equation

$$\frac{dn_{N_2O}}{dt} = -k_{N_2O} n_C \eta_{N_2O} p_{N_2O}, \quad (2)$$

where: k_{N_2O} – rate constant, $(sPa)^{-1}$; n_C – contents of solid carbon in the char sample,

mol; η_{N_2O} – effectiveness factor (fraction of a particle's volume available for reaction); p_{N_2O} – partial pressure of N_2O in the gas mixture inside the reactor, Pa.

Because the value of the rate constant k_{N_2O} should be determined from Equation (2), then for porous char particles, two cases must be considered: the reaction can take place either uniformly within the whole particle, so $\eta_{N_2O} = 1$, or only a fraction of the particle is available for the reaction and $\eta_{N_2O} < 1$. Both cases will be allowed during investigations if for the experimental conditions, the rate of

reaction (1) is considered to be controlled by both the heterogeneous kinetics and by the rate of diffusion of N_2O inside the pores, so N_2O concentration within a particle is not uniform and the effectiveness factor $\eta_{N_2O} \leq 1$. Assuming spherical char particles, it is possible to calculate the effectiveness factor from [17]

$$\eta_{N_2O} = \frac{3}{Th} \left(\frac{1}{\tanh(Th)} - \frac{1}{Th} \right). \quad (3)$$

The Thiele modulus (Th) is described by the relation

$$Th = \frac{d}{2} \sqrt{\frac{k_p}{D_e}}, \quad (4)$$

where: d – particle diameter, m; p – total pressure, Pa; $k = k_{N_2O} \rho_C (1 - \varepsilon_C) / \gamma M_C$; M_C – molecular mass of carbon, kg kmol⁻¹. The expression $\gamma = p/RT$, where: R – gas constant, J(kmol K)⁻¹; T – temperature, K. The effective diffusion coefficient D_e , m²s⁻¹ is a function of

the molecular diffusivity D_{N_2O-He} , the Knudsen diffusion coefficient D_{K,N_2O} , and the tortuosity τ of the char pores in (Laurendeau [18])

$$D_e = \frac{\varepsilon_C}{\tau^2} \left(\frac{1}{D_{N_2O-He}} + \frac{1}{D_{K,N_2O}} \right)^{-1}. \quad (5)$$

The tortuosity was assumed as for the parent coal (Tomeczek and Mlonka [19]). An iterative procedure was used in the evaluation of the rate constant k_{N_2O} using Equation (2) because the Thiele modulus is a function of k_{N_2O} . To start the procedure, a value $\eta_{N_2O} = 1$ was used. The rate of N_2O reduction was calculated from the difference between the initial and final numbers of N_2O moles in the reactor and the isothermal reaction time. The partial N_2O pressure used in Equation (2) was assumed to be an arithmetic mean of p_{N_2O} during the whole experiment.

RESULTS AND DISCUSSION

The effectiveness factor was calculated assuming a mean particle diameter $d = 0.9$ mm, a mole fraction of N_2O outside a char particle 300 ppm and the rate constant k_{N_2O} for $\eta_{N_2O} = 1$. Then an iterative procedure yielded final experimental values of the rate constant k_{N_2O} as presented in Figure 2. Thus, the rate constant could be assumed to be independent of pressure and one straight line was drawn in Figure 2. The slope corresponds to the activation energy of 75 kJ/mol. Further details are given in Table 3.

This procedure converged quickly, and the final values of the calculated effectiveness factor as a function of the total pressure are

presented in Figure 3 for two temperatures. Within the examined temperature range, η_{N_2O} only slightly depends on pressure for all three chars.

The values found for η_{N_2O} are smaller than one and so indicate that heterogeneous reduction of N_2O by char is controlled both by chemical kinetics and diffusion of N_2O in char particle's pores. This confirms the results of Johnsson et al. [11] for char particles above 1 to 2 mm at 1076 K and 0.1 MPa. Croiset et al. [14] noticed the influence of the total pressure on k_{N_2O} within the range of 0.2 – 1.0 MPa. However, this influence was not confirmed in the present work.

Table 3. Reaction rate constant $k_{N_2O} = k_0 \exp(-E/RT)$ $N_2O + C \rightarrow N_2 + CO$ **Tablica 3.** Konstanta brzine reakcije $k_{N_2O} = k_0 \exp(-E/RT)$ $N_2O + C \rightarrow N_2 + CO$

| Authors | Temperature | Pressure | E | k_0 | Remarks |
|-------------------------|--------------------|------------|---------------|----------------------------|---|
| | <i>1.1.1.1.1 K</i> | <i>MPa</i> | <i>kJ/mol</i> | <i>(s Pa)⁻¹</i> | |
| De Soete [7] | 800 - 1300 | 0.1 | 101 | $6.4 \cdot 10^{-1}$ | d = 35-50 μ m char from PROSPER coal |
| Goel et al. [9] | 1023 - 1123 | 0.1 | 141 | $4.8 \cdot 10^3$ | d = 4mm, NEWLANDS coal |
| Chen et al. [10] | 873 - 1173 | 0.1 | 137 | $1.3 \cdot 10^{-6}$ | $A = 5 \cdot 10^6 \text{ m}^2 \text{ kg}^{-1}$, d = 3-4.5mm, char from SKULL coal |
| Croiset et al. [14] | 850 - 1200 | 0.2 | 78 | $2.1 \cdot 10^{-3}$ | $A = 50 \text{ m}^2 \text{ kg}^{-1}$ based on external surface area, d = 90 – 106 μ m, char from WESTERHOLT coal |
| | | 0.6 | 85 | $3.0 \cdot 10^{-3}$ | |
| | | 1.0 | 91 | $4.3 \cdot 10^{-3}$ | |
| De Soete et al. [15] | 800 - 1200 | 0.1 | 101 | $9.4 \cdot 10^0$ | d = 35-50 μ m char from PROSPER coal |
| | | 0.2 | 78 | $5.3 \cdot 10^{-3}$ | d = 90-106 μ m char from WESTERHOLT coal |
| This work | 973 - 1173 | 0.2-1.0 | 75 | $4.0 \cdot 10^{-5}$ | d = 0.8-1.0 mm chars from: SIERSZA, JANINA and PIAST coals |

The influence of pressure on k_{N_2O} for the WESTERHOLT char as measured by Croiset et al. [14] is presented in Figure 4. The figure shows that the difference between k_{N_2O} for SIERSZA, JANINA, PIAST chars and WESTERHOLT char investigated by Croiset et al. [14] within a similar pressure range is within experimental uncertainty.

Because the experiments were conducted for small char particles sized 95 μ m, η_{N_2O} was close to one and the influence of pressure on

k_{N_2O} observed by Croiset et al. [14] cannot be eliminated. In their later work, the same authors (de Soete et al. [15]) did not reject the dependence of the reaction rate constants on the total pressure for chars produced under the same conditions, what can be seen in Figure 4.

Chen et al. [10] noticed for temperatures 873 – 1173 K, a particle diameter of 3–4.5 mm and the pressure 0.1 MPa for SKULL char, the lowest values of the kinetic factor.

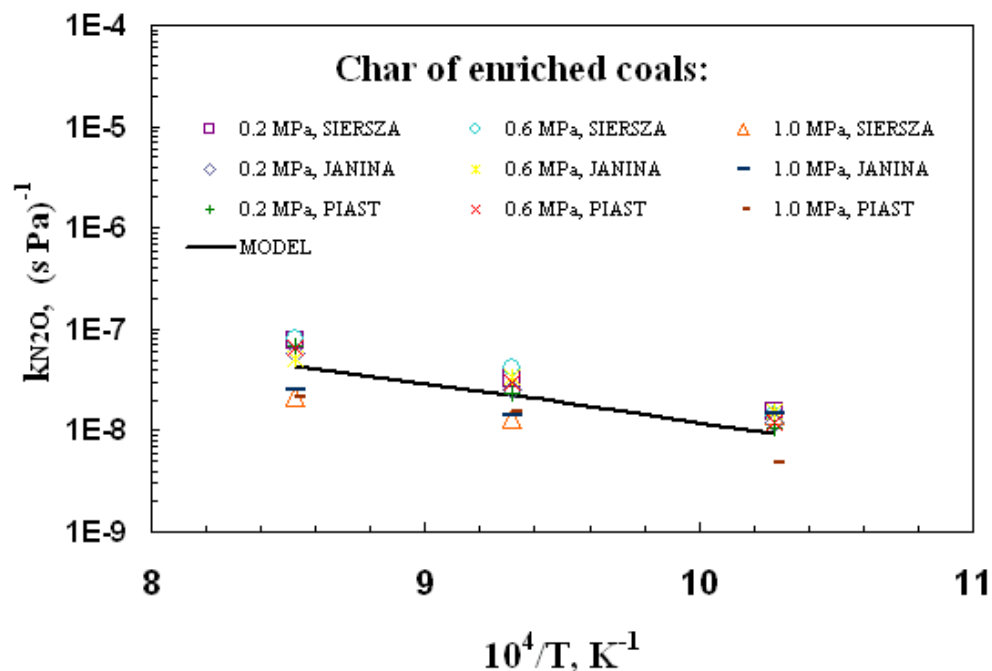


Figure 2. Reaction rate constant k_{N_2O} $N_2O + C \rightarrow N_2 + CO$ for the particle effectiveness smaller than one

Slika 2. Konstanta brzine reakcije k_{N_2O} $N_2O + C \rightarrow N_2 + CO$ za učinkovitost čestica manjom od jedan

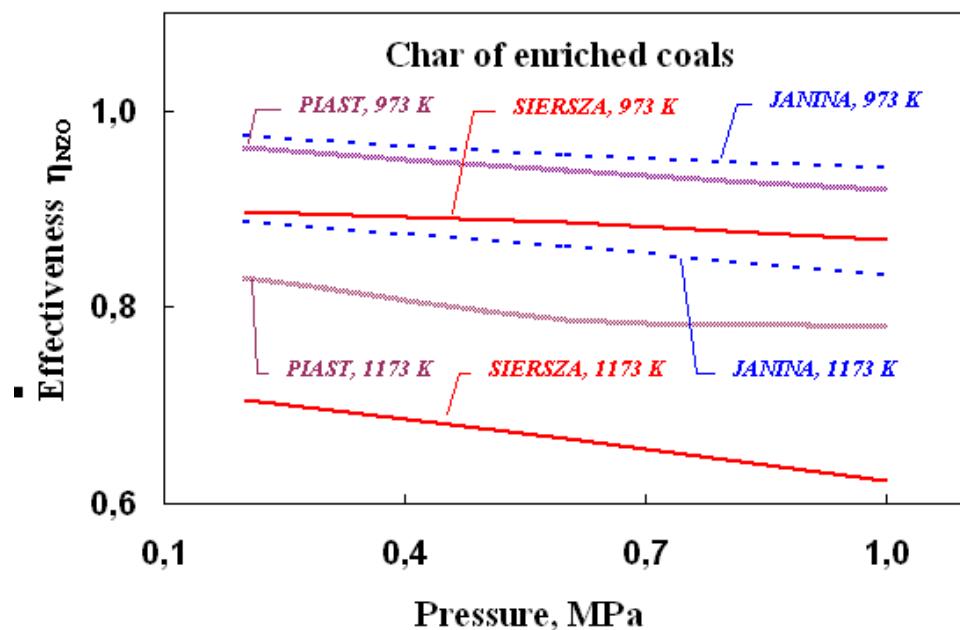


Figure 3. Effectiveness factor as function of pressure for: $N_2O = 300$ ppm, $d = 0.9$ mm and k_{N_2O} from Table 3

Slika 3. Faktor učinkovitosti kao funkcija tlaka za: $N_2O = 300$ ppm, $d = 0.9$ mm i k_{N_2O} prema tablici 3

It must be noticed that it is very difficult to compare directly the results obtained here with those from the literature sources, mainly because of the different units applied. It was decided then to recalculate the available measurements into common units of $(\text{s Pa})^{-1}$, assuming char properties given in the quoted references.

The results are presented in Table 3. This procedure brings new uncertainty caused by the value of a char's internal surface area. The differences among the rate constants are caused mainly by the properties of chars used in the experiments with some contribution of the experimental method. A common feature of the investigated chars is that all were produced at the atmospheric pressure.

Most striking, however, is the value of the activation energy. For the first three experiments listed in Table 3, the activation energy is within the range of 101-141 kJ/mol, while recent studies [14] and this work

indicate lower values of activation energy, 75-91 kJ/mol. The controlling effect of both the chemical reaction kinetics and internal pore diffusion, found during the present work, justifies an activation energy about half that value compared to the cases where very small char size was used and the reaction was controlled only by chemical kinetics, while the former value 78 kJ/mol for small particles is difficult to substantiate [14, 15].

Croiset et al. [14] and de Soete et al. [15] found that molecular nitrogen released from char-N originated from N_2O reduction rather than from reducing NO. Because $k_{\text{N}_2\text{O}}$ does not depend on pressure, it seems possible to use results from the experiments conducted at the atmospheric pressure for modelling pressurised conditions, and vice versa. This should be understood in the way that the properties of char are determined by the pressure of its formation during carbonization.

CONCLUSIONS

- The rate constant of the overall reaction $\text{N}_2\text{O} + \text{C} \rightarrow \text{N}_2 + \text{CO}$ is independent of pressure if chars are produced under the same conditions.
- Within the analysed ranges of pressure

and temperature, reduction of N_2O by SIERSZA, JANINA and PIAST chars is controlled by both chemical kinetics and diffusion in pores, with an activation energy of 75 kJ/mol.

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